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The effect of natural rubber on the biodegradability of PHBV

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Abstract

Biodegradable plastics can break down into water, carbon dioxide, and/or methanol by microorganisms, offering several advantages over conventional plastic, such as waste reduction, source reduction, and energy saving. PHBV and natural rubber are individually biodegradable, but the rubber-PHBV blends have never been studied to assess this property. It is hypothesized that the addition of rubber retains PHBV biodegradability. Therefore, the biodegradability of PHBV/rubber blends was studied in an aerobic composting system at 58 ℃. The result has shown that the pure PHBV has much higher degree of biodegradability than that of the rubber-PHBV blend. The addition of the natural rubber did improve the elasticity of the PHBV, but it weakened the feature of the biodegradability of the PHBV. In the future, a better weight fraction of the natural rubber in the blend is need to be found.

Acknowledgements

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2. Introduction

2.1 Background Brief Introduction

More than 90% of the plastics currently used for food packaging are made from conventional plastics, which are petroleum based and non-biodegradable. Currently, the bioplastics account for less than 1% of the global plastic production. The wide use of the conventional plastics causes environmental concerns due to their non-biodegradability and oil consumption. Therefore, there is increasing research interest in bioplastics.

Polyhydroxybutyrate-co-valerate (PHBV) is produced from carbon-rich resource through microorganism fermentation. Currently bacteria Alcaligenes eutrophus is regarded as the main producer of PHBV with the feedstock of propionic acid and glucose. PHBV can be decomposed completely into water and carbon dioxide in aerobic condition. In some research, the biodegradability was evaluated by visual analysis, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA).

2.2 Principle and Expected Results

PHBV has limited industrial applications mainly due to its brittleness. Natural rubber has been incorporated into PHBV to improve its toughness. As natural rubber is bio-based and biodegradable, it is hypothesized that the addition of rubber can retain the biodegradable characteristics of PHBV. In other words, both pure PHBV and the PHBV-rubber blend will be

biodegradable. Thus, this study aimed to investigate the biodegradability of PHBV/natural rubber blend by measuring the amount of carbon dioxide produced in the composting vessel during the biodegradation process.

2.3 Reference

1. Home › News Updates › Packaging Applications Driving Growth of Biodegradable Plastics." Packaging-Applications-Driving-Growth-of-Biodegradable-Plastics, Markets and Markets , 14 June 2011, www.marketsandmarkets.com/Newsupdate/packaging-applications-driving-growth-of-biodegradable-plastics.asp.--

2. Batista, K.C., Silva, D.A.K., Coelho, L.A.F. et al. J Polym Environ (2010) 18: 346. https://doi.org/10.1007/s10924-010-0238-4--

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3. Methodology

3.1 List of the reagents

3.1.1 Composting, a mixture of

- 109.1 g soil (obtain from the COM-TIL COMPOST facility at Columbus and include biodegrader)
- 320 g sea sand, to keep the system in high water holding capacity.
- 118.81 g water, to keep the compost moist
- 0.186 g lime, to adjust the pH of the compost to 7-9.
- Two types of testing material, 7 g pure PHBV and 7 g PHBV-rubber blend (15 weight percent). The testing samples were cut into many small pieces (square in 5 mm $*$ 5mm) and one big piece (square in 1.2 mm $*$ 1.2mm). The testing samples were placed in composting vessels with circulating air and kept at 58 °C in a water bath.

3.1.2 0.025 M Barium hydroxide solution, to remove CO_2 in the air

3.1.3 0.5 M H_2SO_4 solution, to trap the produced ammonia.

3.1.4 0.05 M HCl solution, titrate the barium hydroxide solution.

3.1.5 Phenolphthalein, acid-base indicator for the titration.

3.2 Apparatus

3.2.1 Water bath (provide constant temperature of 58℃)

3.2.2 Glass vessels (contain compost, barium hydroxide solution and sulfuric acid solution)

3.2.3 Glass tube

3.2.4 Burette (used to do the acid-base titration)

3.2.5 Air Supply (provide inlet air)

3.3 The brief figure of the experiment

Figure 3-1: the brief figure of the experiment

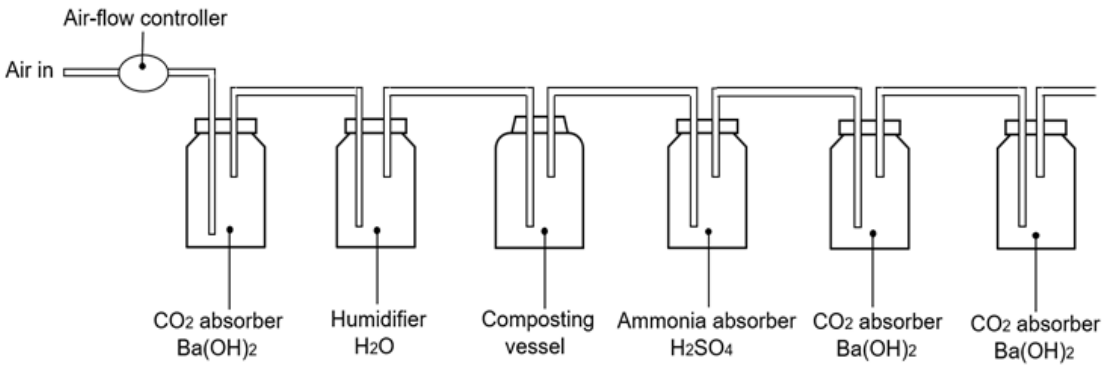


Table 3-1: the volume and concentration in Figure 2-1

Bottle #	CO_2 absorber $Ba(OH)_2$	Humidifier H_2O	Composting Vessel	Ammonia Absorber	CO_2 absorber $Ba(OH)_2$	CO_2 absorber $Ba(OH)_2$
Volume(ml)/Concentrate(M)	250/0.025	250/--	250/--	500/1	250/0.025	250/0.025

3.4 Process of the experiment

3.4.1 Build up the composting system

Three sets of the testing group (two 500-mL-Erlenmeyer flasks and four 250-mL-Erlenmeyer flasks for each set) and the rubber stopper with two holes inserted with the glass tubes were prepared. Natural rubber tubes were used to connect the six flasks for each set. In each set, the two 500-mL Erlenmeyer flasks contained compost (~550g) and barium hydroxide, respectively. The other reagents were included in the four 250-ml Erlenmeyer flasks. The detailed assignment and the order are shown in figure 2-1. The compost in the first set of the testing group should include no testing material, i.e., blank control. The compost in other two sets should include 7 g of rubber-PHBV blend and 7 g of pure PHBV, respectively. The compost had a moisture content of 31%, pH of 7-9, volatile solid of 71.43% (the volatile solid is the material which was volatilized during the incineration of the composting), and ash of 28.57% (the ash is the residue after the incineration of the composting).

3.4.2 Titration

The amount of the CO_2 produced in the composting vessel was measured through titration. This process was operated approximately three times a week after the measurement device was set up. For each titration, 20 ml barium hydroxide solution was extracted from the 500-ml Erlenmeyer flask (CO_2 absorber) of each set of the testing group to each 150 ml-beaker

respectively. several droplets of phenolphthalein were added in those beakers and 0.05 M HCl solution was dropped into those beakers via the burette. Once the pink color in those beakers was fade, the titration should be stop..

3.4.3 Calculation

The biodegradability was calculated by measuring the amount of the CO_2 produced in the composting vessel. The CO_2 precipitated barium hydroxide solution in the CO_2 trap vessel.

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 \downarrow + H_2O \qquad \textit{Equation 3-1}$$

The remaining OH^- can be measured by titration using 0.05M HCl solution xxx and the absorbed CO_2 was calculated as below:

$$\left(2 * C_b * \frac{V_b}{C_a} - V_a * \frac{V_b}{20}\right) * C_a * 22 = amount\ of\ absorbed\ CO_2 \qquad \textit{Equation 3-2}$$

where

C_a=concentration of HCl=0.05 M

C_b=concentration of $Ba(OH)_2$ =0.025 M

V_a=volume of HCl used in titration

V_b=volume of $Ba(OH)_2$ =500 ml

The biodegradability of testing material was calculated as follow.

$$Degree\ of\ biodegradation = \frac{Total\ amount\ CO2\ in\ testing\ vessel - total\ amount\ CO2\ in\ blank\ vessel}{ThCO_2}$$

Equation 3-3

Where

$\mathrm{ThCO2} = \mathrm{m} * w_C * \frac{44}{12}$ (m: mass of test vessel; w_C: mass fraction of the Carbon)

($ThCO_2$ is the theoretically total evolved amount of the CO_2 produced by the composting in testing vessel)

4. Result

4.1 Experimental data

This experiment lasted for 53 days and the accumulated CO_2 amount is as below. The biodegradability of the PHBV-rubber blend was 14.84% and that of the pure PHBV was 24.65%. The accumulated amount of CO_2 produced in each day for the two testing materials were shown in table 1, table 2 and figure 1.

Table 4-1 the accumulated amount of CO2 produced from the rubber-PHBV blend(left)

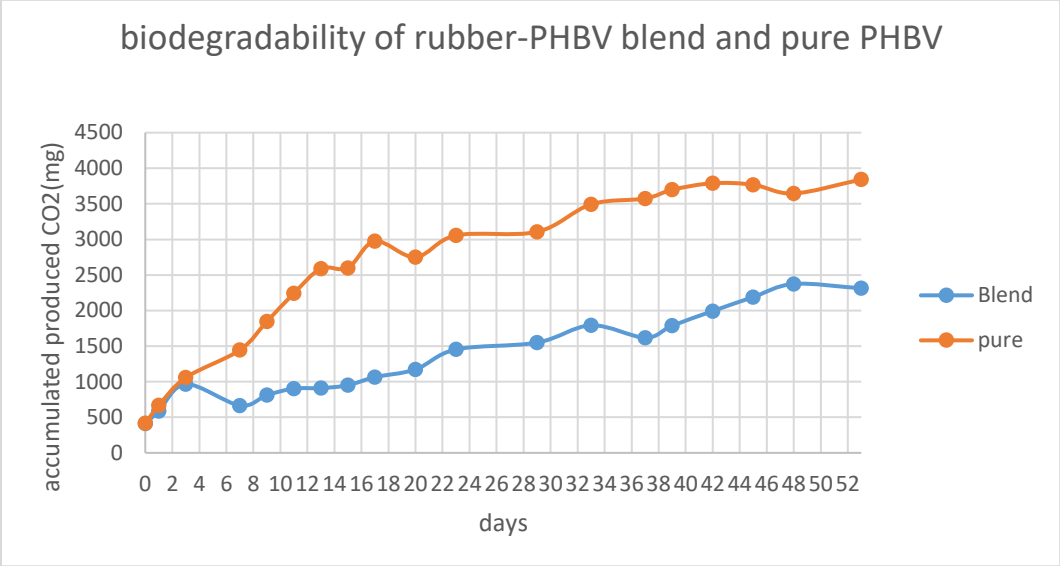
Table 4-2 the accumulated CO2 produced by the pure PHBV (right)

Day	accumulated CO_2 produced
0	411.75
1	589
3	965.625
7	665.625
9	810.975
11	902.975
13	910.55
15	950.575
17	1065.2625
20	1172.325
23	1453.7375
29	1549.3375
33	1792.4625
37	1618.9625
39	1786.5875
42	1992.65
45	2189.775
48	2373.775
53	2313.1375

Days	accumulated CO_2 produced
0	414.5
1	667.375
3	1057.75
7	1445.25
9	1845.25
11	2242.5
13	2589.5625
15	2599.75
17	2975.275
20	2750.275
23	3056.575
29	3105.7
33	3493.2
37	3574.075
39	3697.7
42	3789.6375
45	3768.1375
48	3645.925
53	3841.3125

The plot of the accumulated CO_2 shown in figure 3-1 was based on the above tables.

Figure 4-1the accumulated CO2 produced by both of two kind of the material



4.2 Physical view of biodegradability

In this test, the biodegradation process was visualized (Figure 3-3).

Figure 4-2 pure PHBV (left) and PHBV-rubber blend (right) at the beginning of the test (7/24)

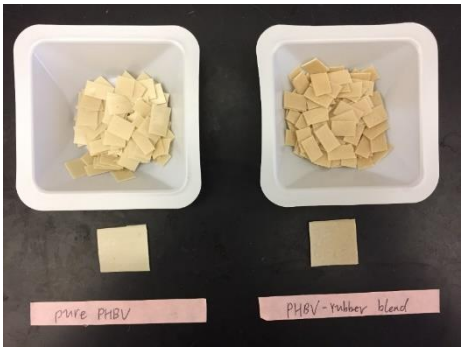


Figure 3-3 and figure 3-4 show the physical change of both pure PHBV and the PHBV-Rubber blend after 22 days and 35 days, respectively.

Figure 4-3 pure PHBV (right) and PHBV-rubber blend (left) at the beginning of the test (8/15)

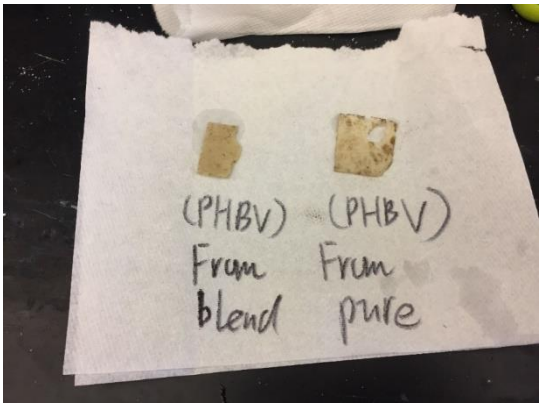
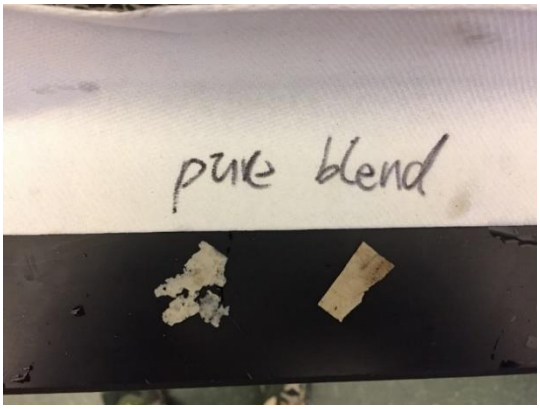


Figure 4-4 pure PHBV (left) and PHBV-rubber blend (right) at the beginning of the test (8/28)



The change of the mass corresponding to different dates was shown in table 4-3.

Table 4-3 the change of mass for the big slice of each kind of the testing material in specific dates

Date	Mass (g)	
	PHBV film	Blend film
7/24	0.446	0.428
7/25	0.448	0.43
8/15	0.2437	0.3684
8/28	0.0784	0.1113

4.3 Analysis of the change of mass and amount of evolved CO_2

After 35 days, the mass of the PHBV film (big slice) was 0.0784 g and that of the blend film (big slice) was 0.1113 g (Table 4-3). The mass loss of PHBV and PHBV/natural rubber blend were 82.42% and 73.99%, respectively. We assumed that all the small slices have the same mass loss percentage as that of the corresponding big slice. Hence, theoretically, each 7 g of PHBV film and blend film had 5.7694 g and 5.1793 g mass loss during the biodegradation process. From figure 3-1, the amount of accumulated CO_2 from the pure PHBV and rubber-PHBV blend were 3493.2 mg and 1792.4625 mg, respectively After 35 days, We also assumed that the all the element of the carbon in the PHBV will be converted to carbon dioxide and the oxygen element in the carbon dioxide was from O_2 in the air supply. Hence the loss of the carbon element in the PHBV films and rubber-PHBV film should be 0.9526 g and 0.4888 g. Based on the data we have calculated before, there were still 4.8186 g and 4.6905 g loss of the biodegraded mass. Hence, those loss of the mass should include the fragments of the testing materials which still left inside the d

5. Discussion

Both PHBV and PHBV/natural rubber blend were biodegradable in aerobic composting system. Rubber addition slowed down PHBV biodegradation due to rubber having high molecular weight molecules and crosslinks (cured by peroxide). During the testing, some leak occurred in the testing device, making the measured amount of produced CO_2 probably lower than the actual amount of produced CO_2. Additionally, the inlet air of the blank control group was not totally CO_2-removed, making the measured CO_2 production higher than the actual CO_2

production and causing the calculated CO_2 production of the two types of testing material lower than actual value. To solve this problem, the CO_2 production of the blank control group was re-measured without any technical issues like leaking. The average amount of CO_2 in the control group was applied to the biodegradability calculation.

6. Conclusion

This experiment followed the guideline of ISO 14855 and the result of the experiment. Based on the result, in the future work, the more optimal weight fraction of natural rubber in the rubber-PHBV blend is needed to balance the mechanical and biodegradable properties of the PHBV/natural rubber blend. The production cost of PHBV needs to be reduced to broaden its industrial applications. The optimized rubber-PHBV is desired to gradually replace the conventional plastics and improve the sustainability of plastic industry.

7. Reference

1. ISO 14855 Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions — Method by analysis of evolved carbon dioxide —Part 2: Gravimetric measurement
2. DIN EN ISO 17556 Determination of the ultimate aerobic biodegradability in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved

8. Appendix A: Raw Data

Titration Recording for blank control group

	V0(HCl)	V1(HCl)	V0(HCl)(replicated)	V1(HCl)(Replicated)	Delta V(HCl)	Delta V(HCl) (replicated)	Average delta V	CO2 produced(mg)
2018/7/27*	9.4	14.09	14.09	19.5	4.69	5.41	5.05	411.125
2018/7/29*	1.8	9.75	9.75	17.7	7.95	7.95	7.95	331.375
2018/8/2*	8.7	17.9	9.75	18.85	9.2	9.1	9.15	298.375
2018/8/4*	5.55	17.51	17.51	29	11.96	11.49	11.725	227.5625
2018/8/6*	13.6	26.5	5.85	18.6	12.9	12.75	12.825	197.3125
2018/8/8*	9.9	21.8	8.5	20.65	11.9	12.15	12.025	219.3125
2018/8/10*	5.06	19.35	7.1	21.3	14.29	14.2	14.245	158.2625
2018/8/12*	2.9	14.9	5	17.2	12	12.2	12.1	217.25
2018/8/15*	9.8	15	15	20.3	5.2	5.3	5.25	405.625
2018/8/18*	15.75	16.4	16.4	17.2	0.65	0.8	0.725	530.0625
	the Ba(OH)2 is contaminated by the H2SO4							
2018/8/24*	5.27	6.1	6.1	6.85	0.83	0.75	0.79	528.275
2018/8/28*	8	10.01	10.01	12.1	2.01	2.09	2.05	493.625
2018/9/1*	3.5	7.95	7.95	12.55	4.45	4.6	4.525	425.5625
2018/9/3*	2.8	14.5	3.1	15.25	11.7	12.15	11.925	222.0625
2018/9/6*	9.9	22.6	0	12.65	12.7	12.65	12.675	201.4375
2018/9/9*	12.8	23.4	8.7	19.2	10.6	10.5	10.55	259.875
2018/9/13*	4.1	21.17	2	19.3	17.07	17.3	17.185	77.4125
2018/9/14, 4:00pm	8.1	23.6	4	19.47	15.5	15.47	15.485	124.1625
2018/9/17*	4.6	15.3	7.3	18.01	10.7	10.71	10.705	255.6125
2018/9/22*	9.1	21.87	7.7	20.4	12.77	12.7	12.735	199.7875

Titration Recording for experimental control group (rubber-PHBV blend)

	V0(HCl)	V1(HCl)	V0(HCl)(replicated)	V1(HCl)(Replicated)	Delta V(HCl)	Delta V(HCl) (replicated)	Average delta V	CO2 produced(mg)
2018/7/25*	9.5	11.7	11.7	14.1	2.2	2.4	2.3	486.75
2018/7/27*	8.3	16.25	16.25	24.5	7.95	8.25	8.1	327.25
2018/7/29*	4.8	5.65	3.15	4.8	0.85	1.65	0.85	526.625
2018/8/2*								
2018/8/4*	9.38	18.4	6	15.5	9.02	9.5	9.26	295.35
2018/8/6*	10.1	21.4	2.5	13.6	11.3	11.1	11.2	242
2018/8/8*	3.6	17.87			14.27		14.27	157.575
2018/8/10*	3.35	16.5	5.88	18.91	13.15	13.03	13.09	190.025
2018/8/12*	8.85	19.2	7.8	18.2	10.35	10.4	10.375	264.6875
2018/8/15*	7.1	15.15	15.15	22.95	8.05	7.8	7.925	332.0625
2018/8/18*	12.58	14.28	14.28	15.75	1.7	1.47	1.585	506.4125
2018/8/24*	17.7	17.89	17.89	18.02	0.19	0.13	0.16	545.6
2018/8/28*	16.9	17.2	17.2	17.4	0.3	0.2	0.25	543.125
2018/9/1*	6	21.5	7.8	23.1	15.5	15.3	15.4	126.5
2018/9/3*	6.9	15.35	15.35	23.8	8.45	8.45	8.45	317.625
2018/9/6*	1.25	5.6	5.6	9.9	4.35	4.3	4.325	431.0625
2018/9/9*	3.5	8.21	8.21	12.8	4.71	4.59	4.65	422.125
2018/9/13*	14.6	17.1	17.1	19.4	2.5	2.3	2.4	484
2018/9/14, 4:00pm								
2018/9/17*	7.6	20.42	1.1	14.1	12.82	13	12.91	194.975

Titration Recording for experimental control group (pure PHBV)

	V0(HCl)(180/500mL)	V1(HCl)	V0(HCl)(180/500mL)(replicated)	V1(HCl)	Delta V(HCl)(180/500mL)	Delta V(HCl)(180/500mL) (replicated)	average delta V	CO2 produced(mg)
2018/7/25	14.1	16.2	16.2	18.5	2.1	2.3	2.2	489.5
2018/7/27	10.8	16.3	16.3	21.5	5.5	5.2	5.35	402.875
2018/7/29	5.8	6.15					0.35	540.375
2018/8/2	500+125mL Ba(OH)2 reacted							687.5
2018/8/4	500 mL Ba(OH)2 done							550
2018/8/6	10	10.1					0.1	547.25
2018/8/8	8	9.95	9.95	11.85	1.95	1.9	1.925	497.0625
2018/8/10	11.25	25.5	1.9	16	14.25	14.1	14.175	160.1875
2018/8/12	7.9	9.7	9.61	10.5	1.8	0.89	0.89	525.525
2018/8/15								
2018/8/18	11.9	12.58			0.68		0.68	531.3
2018/8/24	14	15.9	15.9	17.7	1.9	1.8	1.85	499.125
2018/8/28								687.5
2018/9/1	8.3	14.6	14.6	20.6	6.3	6	6.15	380.875
2018/9/3	4.4	14.5	14.5	24.5	10.1	10	10.05	273.625
2018/9/6	3.95	12.45	12.45	20.9	8.5	8.45	8.475	316.9375
2018/9/9	1	13.6			12.6		12.6	203.5
2018/9/13	11.7	24.97	0.8	14.6	13.27	13.8	13.535	177.7875
2018/9/14, 4:00pm								
2018/9/17	0.4	4	4	7.6	3.6	3.6	3.6	451

9. Appendix B: Safety and Chemical Waste disposal

A. Operational Hazard
   - Chemical Corrosivity
     - In this project, barium hydroxide is a strong base hydrochloride acid do harm to the human skin. When make those two solutions, be avoid spilling to the skin.
   - Hot Water from Water Bath
     - The reaction of microbe and testing material in the composting vessel should keep the constant temperature about 58℃ and the water in the bath is easy to be evaporated. Hence water should keep being refilled to be avoid running out of the water.

B. Required Personal Protect Equipment
   - Thermal gloves
   - Goggle
   - Lab coat (anti-radiation is best)
   - Shoes which cover toes

C. Emergency Action Plan
   - Fire
     - Follow the exit and evacuate from the building by the stair.
   - Loss of Power
     - Use the emergency shutdown of all the device
     - Follow the project advisor for further instruction.

D. Chemical Waste Disposal
   - Labeling
     - Write the all the name of the chemical wastes on the label and stick it on the disposal tank.
   - Take the tank away

- Frequently contact the staff to cycle the chemical waste